

**CORROSION PROTECTION FOR METALS IN CEMENTITIOUS MATERIAL
AND METHOD OF APPLYING AND MAKING THE SAME**

5 CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority to U.S. Provisional Patent Application Serial No. 60/424,516, filed 7 November 2002, entitled "Lithium Nitrate as a Corrosion Inhibitive Admixture for Concrete and Related Methods of Making and Using the Same," the entire disclosure of which is hereby incorporated by reference herein.

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BACKGROUND OF THE INVENTION

The present invention relates to reduction of corrosion in rebar and/or other metals embedded in cementitious material, which among other things, can be important to minimize long-term infrastructure costs. The corrosion of reinforcing metals in cementitious material is estimated, for example, to affect more than 50 percent of the 575,000 bridges in the United States.

20 BRIEF SUMMARY OF THE INVENTION

Certain exemplary embodiments can comprise a method for preventing, inhibiting, and reducing the corrosion of metals embedded in cementitious material. The reduced corrosion rate therefore increases the life expectancy of the structures formable from cementitious material. Some exemplary structures formable from the cementitious material include the following, but are not limited thereto, pillars, bridge decks, bridges, road decks, roads, houses, buildings, pilings, railroads, warehouses, piers, parking structures, wharves, or any other structures desired or required, etc. The method can comprise manufacturing lithium nitrate. The method can further comprise providing

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lithium nitrate for addition to the cementitious material at an effective dosage rate. The dosage rate can be between about 0.01 gram moles per cubic foot of cementitious material and about 100 gram moles per cubic foot of cementitious material. In other exemplary embodiments the effective dosage rate can be greater than 100 gram moles per cubic foot of cementitious material as desired and/or required.

An embodiment provides a method for preventing, inhibiting or reducing the corrosion of metals embedded in cementitious material. The cementitious material manufacturable from a process comprising the activities of: manufacturing lithium nitrate; and providing the lithium nitrate for addition to the cementitious material at an effective dosage rate.

An embodiment provides a method for preventing, inhibiting or reducing the corrosion of metals embedded in concrete or any other cementitious material. The concrete or cementitious material manufacturable from a process comprising the activities of: obtaining lithium nitrate; and mixing the lithium nitrate with the concrete or cementitious material at an effective dosage rate.

An embodiment provides a method for preventing, inhibiting or reducing the corrosion of metals embedded in grout. The grout manufacturable from a process comprising the activities of: obtaining lithium nitrate; and mixing the lithium nitrate with the grout at an effective dosage rate.

An embodiment provides a method for preventing, inhibiting or reducing the corrosion of metals embedded in mortar. The mortar manufacturable from a process comprising the activities of: obtaining lithium nitrate; and mixing the lithium nitrate with the mortar at an effective dosage rate.

An embodiment provides a method for preventing, inhibiting or reducing the corrosion of metals embedded in cementitious material. The cementitious material manufacturable from a process comprising the activities of: obtaining lithium nitrate; and applying the lithium nitrate to the surface of the cementitious material at an effective dosage rate.

An embodiment provides a method for preventing, inhibiting or reducing the corrosion of metals embedded in cementitious material. The cementitious material manufacturable from a previously heated Portland cement composition. The Portland cement manufacturable from a process comprising the activities of: obtaining lithium
5 nitrate; and admixing the lithium nitrate with the Portland cement composition at an effective dosage rate.

An embodiment provides a method for preventing, inhibiting or reducing the corrosion of metals embedded in cementitious material. The cementitious material comprising a Portland cement composition. The Portland cement composition creatable
10 from a method comprising the activities of: obtaining lithium nitrate; admixing the lithium nitrate with the Portland cement in an amount sufficient to inhibit the corrosion of metals; and heating the material to form a Portland cement clinker.

An embodiment provides a composition comprising: a concrete or cementitious material comprising between about 0.01 gram moles (or lower) of lithium nitrate per cubic
15 foot of concrete to about 100 gram moles (or higher) of lithium nitrate per cubic foot of concrete or cementitious material.

An embodiment provides a composition comprising: a grout comprising between about 0.01 gram moles (or lower) of lithium nitrate per cubic foot of grout to about 100 gram moles (or higher) of lithium nitrate per cubic foot of grout.

20 An embodiment provides a composition comprising: a mortar comprising between about 0.01 gram moles (or lower) of lithium nitrate per cubic foot of mortar to about 100 gram moles (or higher) of lithium nitrate per cubic foot of mortar.

An embodiment provides a composition comprising: a cementitious material comprising an effective amount lithium nitrate per cubic foot of cementitious material for
25 inhibiting the corrosion of metals embedded in cementitious material.

These and other objects, along with advantages and features of the invention disclosed herein, will be made apparent from the description, drawings, and claims that follow.

BRIEF SUMMARY OF THE DRAWINGS

The present invention and its wide variety of potential embodiments will be more readily understood through the following detailed description, with reference to the accompanying drawings in which:

5 **FIG. 1** is a bar chart illustrating test results of an exemplary embodiment;

Fig. 2 is a flow diagram of an exemplary embodiment of a method of use 2000 of lithium salts;

FIG. 3 is a flow diagram of an exemplary embodiment of a method of use 3000 of lithium salts; and

10 **FIG. 4** is a flow diagram of an exemplary embodiment of a method of use 4000 of lithium salts.

DETAILED DESCRIPTION OF THE INVENTION

15 **FIG. 1** is a bar chart illustrating test results of an exemplary embodiment. The addition of lithium nitrate to concrete can be an effective means of reducing, inhibiting, and preventing the corrosion of metallic reinforcement members encased in the concrete. The bar chart illustrates experimental results measuring the corrosion of metals encased in concrete, wherein one of a plurality of different substances is admixed with the concrete.
20 In particular, the chart reveals the survivability of wires after 100 weeks of measuring resistance change for all admixed concrete. The Line (arrows) represents the control.

 As used herein, the term “metal” means any metal used to improve the structural properties of a cementitious material. Metals can comprise steel, rebar, cast iron, copper, brass, zinc, aluminum, and/or any alloy thereof, etc. As used herein the term “cementitious
25 material” means any hardenable concrete, cement, mortar, pozzalanic cement, other suitable material, and/or grout, or any combination thereof, etc. that can be hardenable from curing. The term “cementitious material” can refer to a dry mix or material before water is added for reaction purposes, a slurried mix after water is added for reaction

purposes, and/or a hardened mix after the slurried mix or material are allowed to cure, or any combination thereof. The "cementitious material" can include any plastic or fluid state. As used herein, the term "pozzalanic cement" means any cement comprising a "pozzalanic" substance. As used herein, the term "pozzalanic" substance means a substance that by itself comprises little or no cementing properties, but in the presence of lime and moisture can comprise cementing properties.

Substances mixed with concrete in the tests reported in Fig. 1 comprise: AMA – aminoethylethanolamine, ATP – 2-aminothiophenol or orthoaminothiophenol, BGP – di-sodium –beta glycerophosphate, CN – calcium nitrite, DS – di-n-butyl sulfoxide, LN – lithium nitrate, NA – Sodium metasilicate, and PA – Phosphonic acid (also known as aminotrimethylenephosphonic acid (AMP) and nitrilotrisphosphonic acid).

Lithium nitrate added at an effective amount of 0.815 gmole/cubic foot of concrete can reduce, inhibit, and prevent corrosion rates of embedded metal significantly as compared to a control sample as illustrated on the bar chart as a line arrow.

FIG. 2 is a flow diagram of an exemplary embodiment of a method of use of lithium salts. At activity 2100 a lithium salt can be manufactured. The lithium salt can comprise lithium nitrate, lithium carbonate, and/or lithium hydroxide, etc.

At activity 2200 the lithium salt can be dissolvable in water to form an aqueous solution. In certain exemplary embodiments, the aqueous solution can be undersaturated, saturated, or supersaturated with respect to the lithium salt.

At activity 2300 the lithium salt can be added to cementitious material. The lithium salt can be added to cementitious material as a dry component, as a component of an aqueous solution, and/or as a constituent of another component such as, for example, Portland cement, etc. The lithium salt can be added at an effective concentration. The effective concentration can be between about 0.01 gram moles per cubic foot of cementitious material and about 100 gram moles per cubic foot of cementitious material. The effective concentration can be any amount within the range such as about: 0.014, 0.1, 0.94, 0.815, 1, 7.899, 28.711, 33, 34.0, 59.822, 89, or 97.323 gram moles per cubic foot of

cementitious material, etc. In other exemplary embodiments the effective concentration can be greater than 100 gram moles per cubic foot of cementitious material as desired or required.

The lithium salt can be blended with other ingredients to form the cementitious material by any technique such as batch mixing and/or continuous mixing. Any mixing equipment can be used for mixing the lithium salt with the other ingredients forming the cementitious mix such as, for example, a ribbon blender, a rotary drum, a rotary kiln, a screw conveyor, a belt conveyor, a truck with a rotating element, and/or any other desired or required mixing or blending apparatus, etc.

FIG. 3 is a flow diagram of an exemplary embodiment of a method of use 3000 of lithium salts. At activity 3100 a lithium salt can be obtained. The lithium salt can be obtained, for example, from a manufacturer, a distributor, and/or a broker, etc.

At activity 3200 the lithium salt can be mixed with other ingredients to form a cementitious material. In certain operative embodiments, when mixed with cementitious material the lithium salt can reduce, inhibit, and prevent rates of corrosion in metals embedded in the cementitious material. In other exemplary embodiments, the lithium salt can act to suppress an alkali silica reaction in the cementitious material. As used herein the term "alkali silica reaction" means a reaction of an alkali in cementitious material with reactive silica comprised in aggregates in the presence of water. The alkali silica reaction can cause deterioration in cementitious material due to the swelling of a gel formed consequent to the reaction. Suppressing the alkali silica reaction can increase the life of cementitious materials by reducing and inhibiting deterioration rates of the cementitious material itself. Reducing and inhibiting the corrosion rate of metals embedded in cementitious material can increase the life expectancy of structures (including for example, but not limited thereto, pillars, bridge decks, bridges, road decks, roads, houses, buildings, pilings, railroads, warehouses, piers, parking structures, and/or wharves) formable from cementitious material.

At activity 3300 the lithium salt can be applied to a cementitious material surface. The lithium salt can penetrate the cementitious material surface and be absorbed into the cementitious material. Lithium absorbed into the cementitious material can be adaptable to reduce, inhibit, and prevent the corrosion rate of metals comprised in the cementitious material as well as acting to suppress the alkali silica reaction.

FIG. 4 is a flow diagram of an exemplary embodiment of a method of use 4000 of lithium salts. At activity 4100 a lithium salt can be obtained.

At activity 4200 the lithium salt can be mixed with a Portland cement. Portland cement can comprise a heated mixture of limestone and clay. In certain exemplary embodiments, the Portland cement raw materials can be prepared to feed a kiln using dry ingredients. In other embodiments, the Portland cement raw materials can be prepared for the kiln by mixing ingredients in a slurry. After passing through the kiln, a Portland cement clinker can be formed. Portland cement clinker can be ground after being formed in the kiln. In certain exemplary embodiments, the lithium salt can be mixed with the Portland cement raw materials prior to the Portland cement raw materials entering the kiln. In other exemplary embodiments, the lithium salt can be added to the Portland cement during grinding or other processing after the Portland cement raw materials have passed through the kiln to form the Portland cement clinker. In certain operative embodiments, lithium nitrate can be mixed with Portland cement in an amount sufficient to provide a molar ratio of lithium to sodium equivalent in the resultant cement clinker of between about 0.01:1 to about 0.1:1. In other exemplary embodiments, the lithium nitrate can be mixed with Portland cement in an amount sufficient to provide a molar ratio of lithium to sodium equivalent in the resultant cement clinker of between about 0.01:1 to about 10:1 or greater as desired or required. Still yet, other resultant cement clinkers are in the range of between about 0.1:1 to about 1:1; about 1:1 to about 5:1; and/or about 5:1 to about 10:1, etc.

At activity 4300 the Portland cement raw materials can be routed through the kiln to be indurated to form a clinker. The Portland cement raw materials can be heated in the

kiln to a temperature in excess of 2,000 degrees Fahrenheit or any temperature as desired. The kiln can use coal, natural gas, and/or fuel oil, or other desired fuel/energy, etc. as sources of energy.

At activity **4400** Portland cement can be added with other ingredients such as sand, gravel, a coarse aggregate, or other suitable material, and/or water, or any combination thereof, etc. to form a cementitious material. The cementitious material can be cast around metal components or other components as desired. Metal components can be used to provide reinforcement, pre-stressing and/or post-tensioning to improve the structural characteristics of the cementitious material. As used herein the term “pre-stressing” the cementitious material means stretching high strength metal cables or strands between two fixed abutments, then casting the cementitious material on and/or in a form that can be placed between the abutments. The cementitious material can cure. The cables can be cut free from the abutments after curing the cementitious material. Pre-stressed cementitious materials can recover, in certain embodiments, when loaded beyond a capacity rating.

As used herein, the term post-tensioning means a method for strengthening concrete using metal strands or bars typically referred to as tendons. The tendons can be placed in the cementitious material. Once the cementitious material has reached a required strength, tension can be applied to the tendons. The tendons can be anchorable in a position after tension is applied to the tendons. In certain embodiments metals used in post-tensioning applications can be encasable in grout. Metals encasable in grout can be better protected from deleterious elements as compared to metals not encasable in grout.

The following publications, patents, patent applications are hereby incorporated by reference herein in their entirety:

1. U.S. Patent No. 6,524,465 B1 to Ashida et al.
2. U.S. Patent No. 6,500,254 B1 to Baxter et al.
3. U.S. Patent No. 6,402,990 B1 to Marazzani et al.
4. U.S. Patent No. 6,342,101 B1 to Miksic et al.
5. U.S. Patent No. 6,340,438 B1 to Lane et al.

6. U.S. Patent No. 6,217,742 B1 to Bennett
7. U.S. Patent No. 6,071,436 to Incorvia
8. U.S. Patent No. 6,033,553 to Bennett
9. U.S. Patent No. 6,022,408 to Stokes et al.
- 5 10. U.S. Patent No. 5,755,876 to Stokes et al.
11. U.S. Patent No. 5,656,075 to Gaidis et al.
12. U.S. Patent No. 5,634,966 to Berke et al.
13. U.S. Patent No. 5,527,388 to Berke et al.
14. U.S. Patent No. 5,422,141 to Hoopes et al.
- 10 15. U.S. Patent No. 5,039,556 to Cogliano et al.
16. U.S. Patent No. 4,466,834 to Dodson et al.
17. U.S. Patent No. 3,826,665 to Hovasse et al.
18. U.S. Patent No. 2,744,831 to McCoy et al.

Still other embodiments will become readily apparent to those skilled in this art
15 from reading the above-recited detailed description and drawings of certain exemplary
embodiments. It should be understood that numerous variations, modifications, and
additional embodiments are possible, and accordingly, all such variations, modifications,
and embodiments are to be regarded as being within the spirit and scope of the appended
claims. For example, regardless of the content of any portion (e.g., title, section, abstract,
20 drawing figure, etc.) of this application, unless clearly specified to the contrary, there is no
requirement for any particular described or illustrated activity or element, any particular
sequence of such activities, or any particular interrelationship of such elements. Moreover,
any activity can be repeated, any activity can be performed by multiple entities, and/or any
element can be duplicated. Further, any activity or element can be excluded, the sequence
25 of activities can vary, and/or the interrelationship of elements can vary. Accordingly, the
descriptions and drawings are to be regarded as illustrative in nature, and not as restrictive.